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Ultrafast mid-infrared spectroscopy by chirped pulse upconversion in 1800-1000cm^{-1} region

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Abstract: Broadband femtosecond mid-infrared pulses can be converted into the visible spectral region by chirped pulse upconversion. We report here the upconversion of pump probe transient signals in the frequency region below 1800cm^{-1}, using the nonlinear optical crystal $AgGaGeS_4$, realizing an important expansion of the application range of this method. Experiments were demonstrated with a slab of GaAs, in which the upconverted signals cover a window of 120cm^{-1}, with 1.5cm^{-1} resolution. In experiments on the BLUF photoreceptor Slr1694, signals below 1 milliOD were well resolved after baseline correction. Possibilities for further optimization of the method are discussed. We conclude that this method is an attractive alternative for the traditional MCT arrays used in most mid-infrared pump probe experiments.

OCIS codes: (040.1880) Detection; (040.3060) Infrared; (320.7150) Ultrafast spectroscopy; (320.7100) Ultrafast measurements; (190.7220) Upconversion.

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1. Introduction

The midinfrared (mid-IR) spectrum from $1000cm^{-1}$ to $3000cm^{-1}$ is a region with rich vibrational information relating directly to molecular structures of most organic molecules. Femtosecond time-resolved UV/Vis pump mid-IR probe spectroscopy is a powerful tool for investigating photo-induced molecular structural and conformational dynamics in fundamental processes in physical chemistry and biology. Recording real time changes in intensity or frequency of vibrational marker modes can provide direct insight into excited states structural dynamics such as biomolecular energy and charge transfer [1–3], bond formation and dissociation [4,5], cis-trans isomerization of a protein's chromophore [6,7], hydrogen network alternation [8,9] and protein folding [10] *et cetera*. To realize high time and spectral resolution simultaneously, sensitive multichannel IR array detectors are used which can cover a broad spectral region. Traditional detector array elements for mid-IR are typically based upon liquid nitrogen cooled photocurrent semiconductors of MCT, InSb, or PbSe [11,12]. Currently in most laboratories, ultrafast IR spectroscopy is performed using 1D

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MCT arrays of 32, 64, or 128 pixels with or without a parallel reference [13–16]. The MCT based detectors provide a limited spectral resolution because their pixels are spaced relatively far apart, they are expensive and have quite complicated electronics.

Alternative methods to detect the mid-IR pulses are optically converting them into the visible region where a sensitive, cheaper detector can be used with many more elements, such as a CCD. Several methods have been demonstrated for measuring mid-IR pulses directly with a visible detector. Pioneering studies by Heilweil *et al* [17,18] realized the first demonstration of direct measurements of picosecond mid-IR pulses in the visible region. In these experiments, the sum-frequency of the mid-IR pulse and a picosecond visible pulse was generated in a thick crystal $LiIO_3$ and resolved with a $4cm^{-1}$ resolution. With the further development of laser sources and materials, in a recent renaissance this method was applied to measure femtosecond mid-IR pulses by upconversion to the visible range in a relatively thin but large area $KNbO_3$ crystal [19]. With this method it was necessary to first spectrally diffract the mid-IR pulse to different places on the $KNbO_3$ crystal surface before it was up-converted with the fundamental pulse of 800nm, and a frequency resolution of around $2cm^{-1}$ was realized. A major breakthrough of this method was realized by the use of a chirped fundamental pulse [20] in a thin Mg doped $LiNbO_3$ crystal, with which a high spectral resolution of $\sim 1cm^{-1}$ could be realized, limited only by the later stages of the experimental setup. This method was subsequently applied to pump probe experiments [21,22] and multidimensional [23–26] mid-IR spectroscopy. More recently, with the chirped upconversion method, a much broader window which covers almost $600cm^{-1}$ was realized [27] with a resolution of $1cm^{-1}$.

So far, the mid-IR chirped upconversion experiments have been realized in the frequency region above $1800cm^{-1}$. However, for most organic compounds, and especially proteins, the frequency region below $1800cm^{-1}$ condenses the most important vibrational information. Previous chirped upconversion experiments have all been limited to investigation of the properties of carbonmonoxide, in several CO-coordinating compounds. Expanding into the lower frequency region has been suggested to be easy to realize, by using other nonlinear optical crystals [20,24]. However, due to several reasons, such as the bandwidth of the upconversion and efficiency of crystal materials transparent below $1800cm^{-1}$, until now, no experimental measurements based on upconversion of mid-IR pulses lower than $1800cm^{-1}$ have been reported. Here, we report chirped upconversion for pump probe experiments to the frequency region below $1800cm^{-1}$. By choosing a high upconversion efficient crystal $AgGaGeS_4$, we demonstrate upconversion-based pump probe experiments down to $1000cm^{-1}$ with high spectral resolution, realizing an important expansion of this method.

2. Principles of chirped pulse upconversion for femtosecond mid-infrared measurements

The key of this method is to use a chirped transient frequency in a pulse of long duration to produce a single narrow spectral component for shifting the broad band mid-IR to the visible region by frequency sum-generation in nonlinear optical crystals, allowing silicon-based detectors to be a viable alternative to the standard IR detectors. For upconversion of an ultrashort mid-IR pulse (without considering for the moment a sample signal field), the process can be easily understood by the schematic illustration depicted in Fig. 1. Generally, a femtosecond mid-IR pulse created by difference frequency generation (DFG) has a pulse duration of ~200fs and a bandwidth of $\sim 100cm^{-1}$. In the time regime, the mid-IR(ΔT~200fs) pulse acts as a time gate, and only a very narrow signal frequency component of the highly chirped fundamental pulse (800nm,~150ps) goes through the crystal and will be added up to the spectrum of the mid-IR pulse, generating the visible pulse without blurring of the spectral resolution. Thus, the upconverted signal is shifted to the visible region with a frequency bandwidth equal to that of the mid-IR pulse. The original mid-IR spectrum can be retrieved by spectrally resolving the upconverted signal with a visible optical spectrometer and a CCD

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detector. The final frequency resolution will depend on the spectrometer and detector channels of the used detection setup.

In practice, when measuring pump probe signals, coherent radiation of the signal field from the studied sample introduced by the excitation pulse, can be much longer than the mid-IR probe pulse, if the spectral features of the sample are narrow. This long-lived radiation field will also be upconverted by the chirped pulse, thus introducing spectral broadening and distortion, decreasing the spectral resolution. However, as previously demonstrated theoretically and experimentally [28], the distortion caused by the sample signal field can be removed with a correction procedure, maintaining the high spectral and sampling resolution.

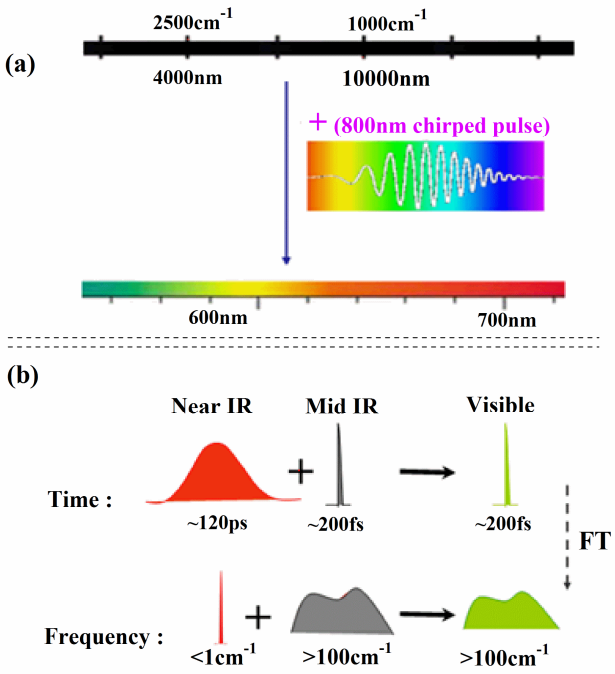

Fig. 1. Schematic illustrations of upconversion the femtosecond mid-IR to the visible region with a highly chirped fundamental pulse of 800nm.

3. Evaluation of nonlinear optical crystals properties for mid-infrared upconversion

The implementation of upconversion of mid-IR pulses to the visible region in a real pump probe experiment faces several challenges. To achieve high time and spectral resolution, sufficient signal to noise ratio, and broad-band upconversion, many factors must be considered, such as the light source and the detection system, especially the material of nonlinear optical crystals. The crystals $LiIO_3$ and KNO_3 used earlier for ps upconversion are not suitable for a fs mid-IR upconversion since much thinner crystals are needed to keep the time resolution and spectral bandwidth, which will make the upconversion efficiency of the crystal too low, especially in the low frequency region below $1800cm^{-1}$. The crystal $LiNbO_3$ doped with Mg previously used for upconversion in the higher frequency region is not transparent for wavenumbers below $1800cm^{-1}$. In previous reports, several crystals such as $AgGaS_2$, $LiInS_2$ were suggested to be suitable for the low frequency region upconversion [20,24]. However, factors such as the phase matching bandwidth, nonlinear efficiency and damaged threshold strongly limit their practical application.

In order to find the best material for upconversion of the mid-IR pulses in the low frequency region, we calculated (program SNLO, http://www.as-photonics.com/snlo) the key parameters for several nonlinear optical crystals based on data available in literature. Figure 2

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shows the phase matching bandwidth and nonlinear efficiency parameters for the best three optional crystals. For the phase matching bandwidth, the crystal $LiInS_2$ is the best, however, its nonlinear upconversion efficiency is the lowest. The one with highest nonlinear upconversion efficiency is the crystal $AgGaGeS_4$, and its phase matching bandwidth is almost the same as of the crystal $LiInS_2$ in the frequency region above 1500cm^{-1}. Below 1500cm^{-1}, the phase matching bandwidth of crystal $AgGaGeS_4$ is just a little less than that of $LiInS_2$. Both the phase matching bandwidth and the nonlinear upconversion efficiency parameters of $AgGaGeS_4$ are better than those of the crystal $AgGaS_2$ in all the frequency region concerned here. We conclude that the crystal $AgGaGeS_4$ is the best material for the mid-IR upconversion measurement both in lower and higher frequency region. Also, the damage threshold of the crystal $AgGaGeS_4$ is higher than of the other two. Indeed, in our experiments we did find that the crystal $AgGaS_2$ is easily damaged by the high intensity of the fundamental pulse. Furthermore, a previous study carried out by Tsubouchi and Momose [29] reported that the upconversion efficiency of $AgGaGeS_4$ is about 30 times larger than Mg doped $LiNbO_3$ in the higher frequency range above 2000cm^{-1}. Thus, it appears that the $AgGaGeS_4$ is the most suitable material so far for mid-IR upconversion. The data presented in this paper are all based on this nonlinear crystal.

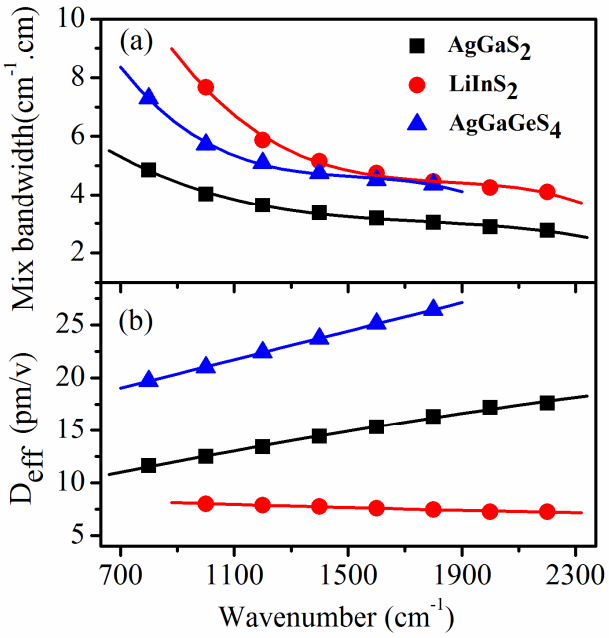

Fig. 2. Calculated phase matching bandwidth parameters in (a) and nonlinear efficiency of sum frequency generation parameters in (b) for three nonlinear optical crystals in mid-IR spectral region.

4. Experimental setup

The laser system (Hurricane, Spectra Physics) is a Ti: sapphire regenerative amplifier with 1kHz repetition rate and fundamental output centered at 800nm, with a bandwidth of 10nm and a pulse duration of ~90fs. The setup for pump probe experiments employing mid-IR upconversion is sketched in Fig. 3. The output fundamental pulse is split in two parts. One part is used for either pumping a homebuilt non-collinear optical parameter amplifier (NOPA) to generate the desired wavelength, or is frequency-doubled in a BBO crystal, and sent to a delay line to be used as excitation pulse. The other part is sent to a optical parametric generator and amplifier (TOPAS, Light Conversion), which consists of two stages: a first

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stage to generate signal and idler pulses in the near IR region, and a second stage where these two pulses are overlapped in a nonlinear crystal $AgGaS_2$ (type I) to generated the difference frequency in the mid-IR. The mid-IR pulses generated in our lab can be tuned in a frequency range from 700cm^{-1} to 3000cm^{-1} with a single window bandwidth of around 100cm^{-1} each.

The chirped pulse for upconversion is picked up from the zero order diffraction of the grating in the compressor. This pulse is normally available in every laser system based on chirped pulse amplification, it is highly chirped and very easily used for upconversion without introduction of additional optics. In our laser system, this uncompressed chirped pulse has a pulse duration of ~150ps, with almost the same bandwidth as the compressed output of ~10nm. The chirped pulse is sent to another delay line, to match its optical path length with that of the mid-IR pulse.

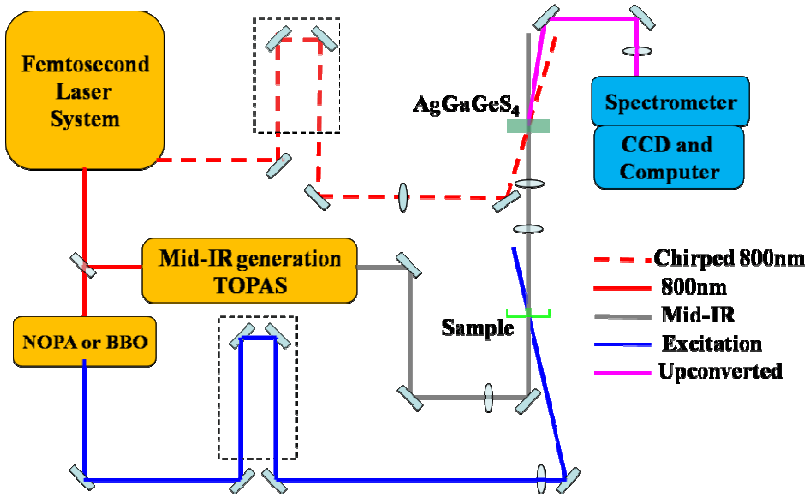

Fig. 3. Scheme of the experimental setup for pump probe measurements and the chirped pulse chirped pulse upconversion mid-infrared.

After interrogation of the sample, the mid-IR pulse is collimated with a 5cm CaF_2 lens, then focused on the crystal $AgGaGeS_4$ with a 20cm CaF_2 lens and overlapped with the chirped pulse. To ensure easy operation and alignment, the chirped pulse was also collimated and then loosely focused with a 50cm fused silica lens, and overlapped under an angle of less than 10° with the mid-IR pulse. The overlapping position of the two beams is before the focusing point of the chirped pulse, where the size of the chirped beam is around 1mm in radius, 5-10 time larger than the mid-IR beam. The nonlinear crystal $AgGaGeS_4$ (type I, ooe) was ordered from CASTECH INC(China, Fujian) with uniform thickness of 0.2mm and 5mm × 5mm area, embedded in an easily rotated holder provided by the company. The crystal has cutting angles of $\theta = 50°$, $\varphi = 0°$, which are the optimized angles for upconversion at 1250cm^{-1}, in order to favor the upconversion in the lower frequency region. All lenses and the crystal $AgGaGeS_4$ were mounted on micrometer to centimeter delay stages, in order to control and choose the proper beam sizes for upconversion. To get the upconverted signal as broad as possible, the lens position of the mid-IR beam was adjusted to get an optimal size inside the crystal where it overlapped with the chirped pulse. The upconverted signal was picked up and collimated, then sent to a ~0.5m spectrometer with a grating of 1200 grooves/mm (modified based on Model 500SM, CHROMEX), which can give a spectral resolution of 0.08nm (~1.6cm^{-1}) at 700nm when using a slit width of 50μm. The spectrally dispersed signal was recorded by a 2048 × 1 pixel silicon CCD camera (model No.S11155-2048; Hamamatsu) and read out by computer for calculation of the transient optical density (OD) changes induced by the excitation pulse.

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5. Results and discussion

Figure 4 shows the mid-IR spectra from 2000cm^{-1} down to 1000cm^{-1} measured with the crystal $AgGaGeS_4$. The top axis shows the visible region to which the mid-IR pulses were upconverted.

The frequency calibration was performed by comparing the absorption spectrum of a 50um polystyrene film, measured in the upconversion system, with the standard absorption spectrum first, and then further optimized by inspection of the location of water vapor absorption lines. In the frequency region above 2000cm^{-1}, the upconversion is much more efficient due to the higher nonlinear efficiency of the crystal, consistent with previous measurements [29]. In the lower frequency region, by increasing the chirped fundamental pulse intensity (to a level still far below the damage threshold of $AgGaGeS_4$), the upconversion is still sensitive enough to get strong up-converted signals. In our current optical configuration with a loosely focusing lens, a 800nm pulse energy of 10μJ and a mid-IR pulse of ~1μJ, the generated upconverted signal is sufficient to saturate the CCD detector. We found that to create damage to the crystal $AgGaGeS_4$, a 30μJ of the chirped pulse energy is needed. Thus, the crystal $AgGaGeS_4$ is suitable for upconversion measurements in the full frequency range from 1000cm^{-1} to 3000cm^{-1} covering the spectral range containing the most important vibrational modes of biological molecules.

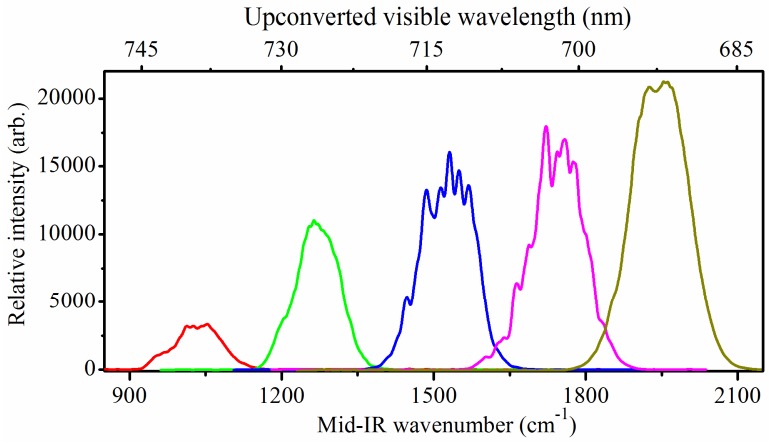

Fig. 4. Upconverted mid-IR spectra by crystal AgGaGeS4 to the visible region and measured by in visible detector CCD. Each spectrum is the average of 1000 pulses. The chirped pulse energy was fixed at around 10μJ.The mid-IR pulse energy was around 1μJ at 2000cm^{-1}. The strong decrease of the upconverted signal in the lower frequency region was caused by the decrease of the nonlinear efficiency of the crystal and the decrease in output power of mid-IR beam.

To demonstrate its practical use in a pump probe measurement, a sheet of 50μm thickness Gallium arsenide (GaAs) crystal was excited at 400nm and the transient decay dynamics measured. Figure 5 shows two representative time traces at a low frequency, 1520cm^{-1}, and at a higher frequency, 2060cm^{-1}. Both of the traces show a fast decay in a few ps, and at 2060cm^{-1} a flat non-decaying phase was observed. The high photon energy excitation at 400nm (3.1eV), causes electrons to be excited from the valence bands to Γ_6 valley with an excessive kinetic energy of ~1.6eV. The fast decays in a few ps in Fig. 5 reflect the intervalley scattering dynamics of $\Gamma_6 \rightarrow X_6/ X_7$ in GaAs, which exhibits a mid-IR absorption introduced by the energetic hot electrons transition $X_6 \rightarrow X_7$, as reported previously [30], the decay decelerated to tens of ps when longer excitation wavelength of 527nm was used. The higher kinetic energy of the hot electrons created by 400nm excitation might accelerate the

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intervalley scattering dynamics $\Gamma_6 \rightarrow X_6/ X_7$ and thus shorten the life time of Γ_6. The non-decaying tail of 2060cm^{-1} trace reflects decay of the free carrier absorption which indicates that recombination of electrons and holes occurs in the nanosecond range [30]. For these large signals in the tens of milliOD, the chirped upconversion system provides a solid measurement of the semiconductor hot electron and carrier dynamics.

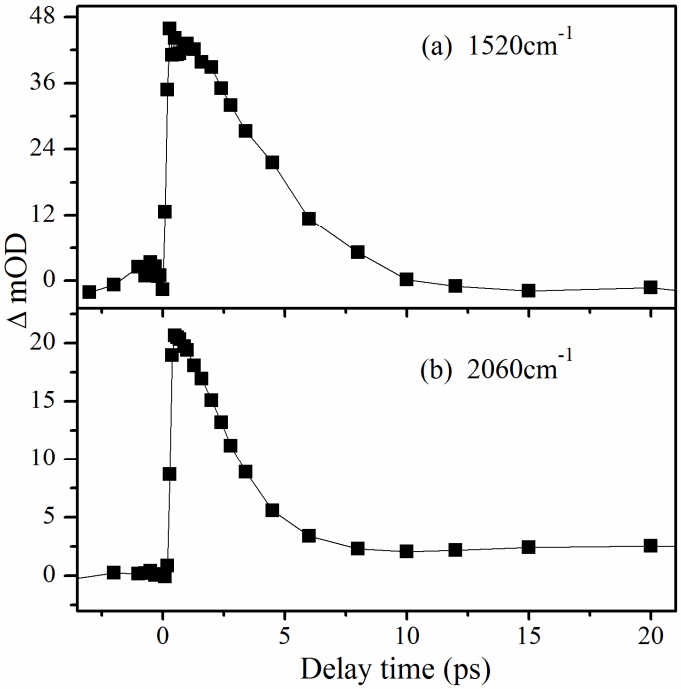

Fig. 5. Pump probe experiment results of a 50μm GaAs demonstrated by the chirped upconversion method. The excitation pulse is at 400nm, ~100nJ.

To demonstrate its use for experiments on dynamics in proteins, that usually show absorption difference signals of less than 1milliOD, we performed an experiment on the blue light absorption photoreceptor Slr1694 protein. The ultrafast vibrational spectroscopic dynamics of this protein were well studied [8,9] with the traditional MCT detectors before. The signals detected with our chirped upconversion system are shown in Fig. 6. We used only one mid-IR probe beam and no reference, thus the baseline fluctuations caused by either the instability of the mid-IR pulses or the upconversion process in the nonlinear crystals are much larger than 1milliOD. Similar baseline fluctuations were also observed in previous upconversion measurements in the higher frequency region [22]. To correct for the baseline, polynomial fits were used and subtracted from the measured signals, as in ref 16. In our current measuring system, as shown in Fig. 6(a), all the pre-zero base lines as at −5, −3 and −1ps could be fitted well with a second or fourth order polynomial. Thus, we assume the same is the case for the delays after time zero. A baseline subtracted spectral signal at 2ps is shown in Fig. 6(b) (blue line). For comparison, the same signal previously measured with a 32 channels MCT was also shown (red line) and normalized to the one measured now. A small distortion appears to have been introduced by the base line subtraction due to the weak signal noise ratio at the edges of the spectral window and the non-determinacy of the positive and negative vibrational peaks of the signal for the polynomial baseline fitting. This point needs further discussion and optimization. Except for that, the baseline subtracted signal accords well with MCT measured signal. In Fig. 6(c) a time trace recorded at 1550cm^{-1} after

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baseline subtraction is shown, it has a lifetime of around 200ps, consistent with the previous measurement [8,9] at this frequency.

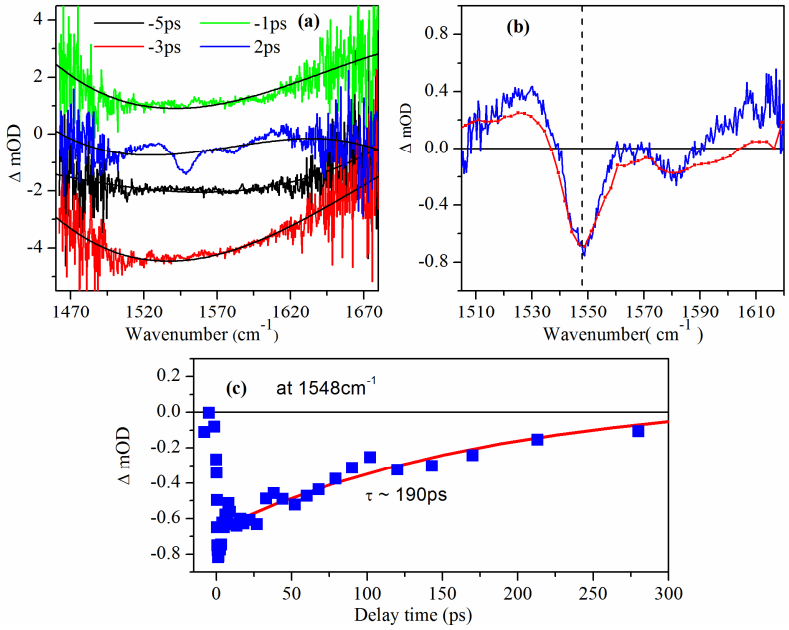

Fig. 6. Pump probe experiments results of BLUF photoreceptor protein Slr1694 demonstrated by the chirped upconversion method in lower frequency region. Excitation pulse was at 400nm, ~400nJ, with polarization parallel to the probe mid-IR pulse. (a) transient spectra at different time-delays without baseline subtraction. (b) transient spectra at pump-probe delay 1ps after baseline subtraction. (c) decay dynamics of the peak 1550cm^{-1} after baseline subtraction.

In the current measurement of the Slr1694 protein sample, the distortion introduced by cross-phase modulation with the sample signal field was not corrected. The distortion to the spectral resolution depends on how much the pulse is chirped and the coherence time of the signal field emitted by the sample. Here, in Slr1694, the population time is long (~200ps Fig. 6(c)), such that its contribution to the spectral width can be ignored, and the spectral width is dominated by the dephasing time. An estimate can be made from the full width at half maximum of the peak at 1550cm^{-1} in Fig. 6(b), which is ~14cm^{-1}. Thus, the coherence time τ_c is ~1.1ps (Assume Gaussian shape as in ref 28, inhomogeneous dephasing in condense phase). For our chirped fundamental pulse of ~150ps, bandwidth of 10nm centered at 800nm, a linear chirp approximation gives the second derivative value of the time phase as $\varphi''(t)\sim 5 \times 10^{-2}$ ps^{-2} (corresponding to a spectral phase second derivative $\varphi''(\omega)\sim 20$ps^2). The upconverted frequency components of the chirped pulse with the signal field can be evaluated by $\varphi''(t)\tau_c$, which is around ~1.8cm^{-1}. Thus the distortion is small and correction is not needed for the Slr1694 sample. This is confirmed by the similar signals to the measured by MCT (Fig. 6(b)). For signals with longer dephasing time, correction will be needed. .An alternative solution is to add a high spectral resolution monochromator to filter out the unwanted spectral components of the chirped pulse before upconversion, as demonstrated in [31].

As already shown in Fig. 6 and mentioned above, the baseline fluctuation is a serious issue for detection of weaker signals. This problem can be partly resolved by using a more stabilized laser system and a more stabilized mid-IR pulse generating system (NOPA/TOPAS). However, improving by this way has its limitation due to the many factors that can induce the baseline fluctuation, such as the excitation energy deposited in the sample which could give rise to a varying thermal diffusion in the solvent, the environmental

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temperature and air fluctuations in which the mid-IR pulse is propagating, etc. A way to permanently resolve the base line fluctuations and improving the signal to noise ratio is to introduce an additional beam as reference, a common method in transient absorption measurements. For the chirped pulse upconversion, we can take advantage of the property that the fundamental pulse is so highly chirped: by splitting the mid-IR beam into two, one for signal one for reference, and sending both to the nonlinear crystal to overlap with the chirped pulse in a symmetrical configuration, but delayed in time by several ps. Thus, the two mid-IR pulse will be upconverted by different frequency components of the chirped pulse. The two upconverted signals will have in the visible region a small frequency shift relative to each other, but have kept the same spectral shape. By designing an appropriate spectrometer, these two similar spectra, separated from each other probably only by several cm^{-1} can be easily imaged such that they match each other on the detector, by tuning a separate mirror or grating in the spectrometer. Such designs are currently under development in our lab.

6. Conclusion

In this study we reported on a method to measure mid-IR absorption difference spectra in the visible region by chirped pulse upconversion using the nonlinear optical crystal $AgGaGeS_4$. This method provides an inexpensive and efficient alternative to conventional multichannel IR measurements using MCT arrays. Using the highly effective crystal $AgGaGeS_4$ we succeeded to extend the upconversion region down to $1000cm^{-1}$ and for the first time demonstrate its use in pump probe experiments in the lower frequency region. Experiments with GaAs showed that the upconversion system is perfect for measurements of signals in the tens milliOD range. Weaker signals, of less than 1 milliOD, suffered from baseline fluctuations. Applying dynamic baseline subtraction, the basic spectral and dynamical properties of a BLUF photon receptor protein were clearly resolved. By further optimization, this upconversion system will be a promising method for pump probe experiments in the mid infrared spectral region.

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